

Supporting information

Multivalent Mg^{2+} , Zn^{2+} and Ca^{2+} Ion Intercalation Chemistry in a Disordered Layered Structure

Seongkoo Kang^{a,b,†}, Kyle G. Reeves^{a,b,†}, Toshinari Koketsu^c, Jiwei Ma^d, Olaf J. Borkiewicz^e,
Peter Strasser^c, Alexandre Ponrouch^{f,g} and Damien Dambournet^{a,b,*}

^a Sorbonne Université, CNRS, Physico-chimie des électrolytes et nano-systèmes interfaciaux, PHENIX, F-75005 Paris, France

^b Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, 80039 Amiens, France

^c The Electrochemical Energy, Catalysis, and Materials Science Laboratory, Department of Chemistry, Chemical Engineering Division, Technical University Berlin, 10623 Berlin, Germany

^d Institute of New Energy for Vehicles, School of Materials Science and Engineering, Tongji University, Shanghai 201804, China.

^e X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, United States

^f Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

^g ALISTORE – European Research Institute, CNRS FR3104, Hub de l'Energie, 15 Rue Baudelocque, 80039 Amiens, France.

Table S1. EDX analysis performed on discharged electrodes. The analysis revealed that the redox reaction is not homogenous with a degree of state of charge that vary depending on where the analysis was conducted (spectrum 1-4). For Mg^{2+} , it can be observed that whatever the degree of magnesiation, the content of chloride is low ruling out the insertion of solvated species such as magnesium monochloride cations.

1st Discharge	vs Mg^{2+}/Mg		vs Ca^{2+}/Ca	
	Mg/Ti	Cl/Ti	Ca/Ti	F/Ti
Spectrum 1	0.22	0.01	0.24	1.14
Spectrum 2	0.16	0.02	0.13	0.97
Spectrum 3	0.38	0.03	0.51	1.14
Spectrum 4	0.20	0.02	0.12	1.05
Average	0.22	0.02	0.25	1.07

Figure S1. X-ray diffraction pattern of the discharged electrode in Ca cell showing the presence of CaF_2 and $CaB_3O_4(OH)_4 \cdot H_2O$.

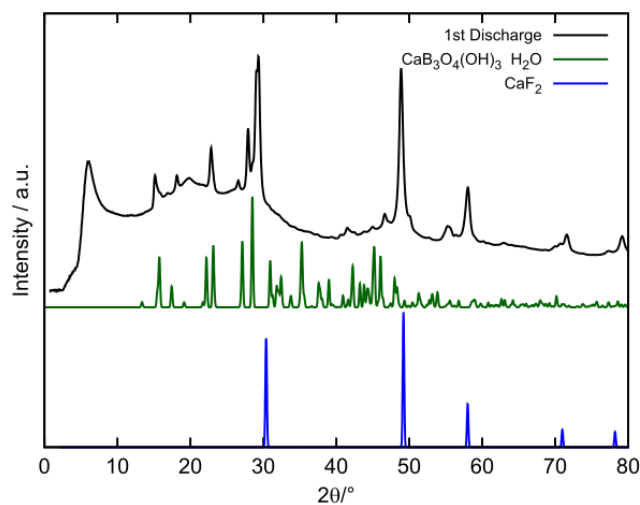


Figure S2. Top: Galvanostatic discharge-charge curves for Ca cells cycled under 5 mA.g^{-1} . **Bottom:** evolution of the coulombic efficiency upon cycling.

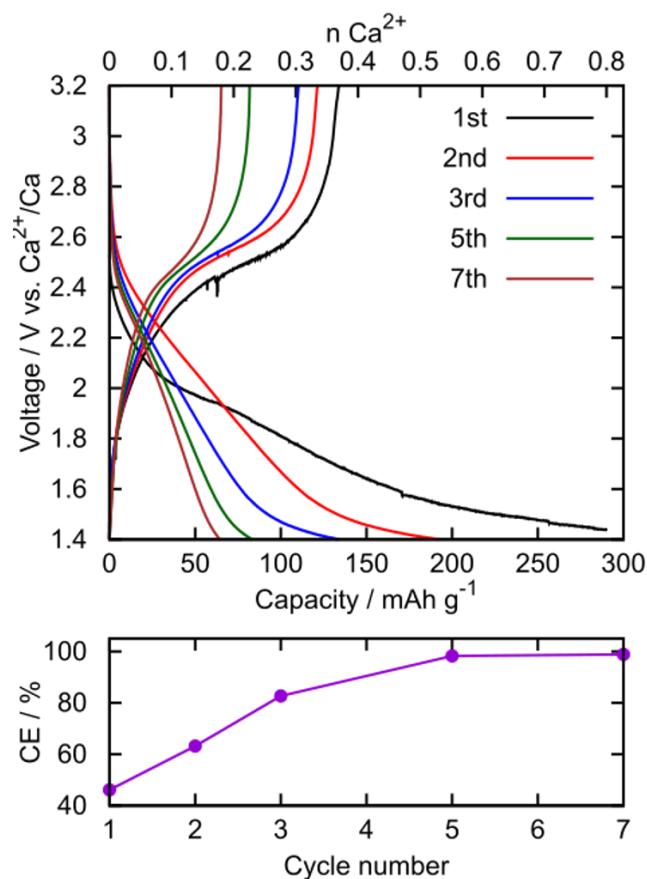


Figure S3. Refinements of the PDF data of the discharged electrode (Mg cells) with and without the presence of Mg^{2+} ions. The quality of the refinement was quantified by the reliability factor weighted R-value, denoted as R_w . The R-value describes the difference between the experimental observation (data) and the calculated value (fit). Both structural models resulted with similar goodness of fit. Both models led to similar goodness of fit, which do not enable to conclude on the Mg-ions locations.

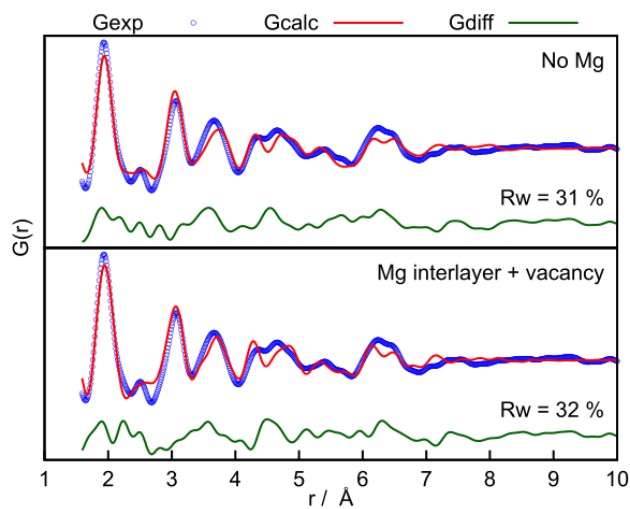
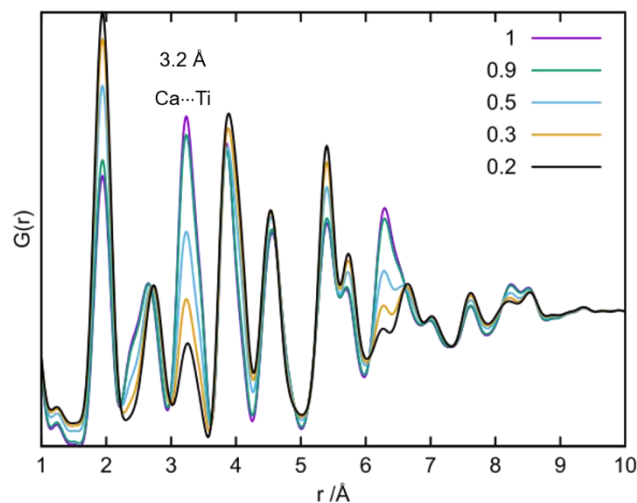


Figure S4. Calculated PDFs of Ca_xTiO_3 with different Ca occupancy (x).



	Li^+		Mg^{2+}	
	DFT	DFT+U	DFT	DFT+U
Vacancy	-35.64	-35.66	-10.86	-18.94
Interlayer	-89.28	-88.87	-90.73	-89.53

Table S2. The energy of formations in units of meV/functional unit for Li^+ and Mg^{2+} at two different configurations (vacancy and interlayer) as shown in Figure 1B and 1C. For each ion, the energy of formation was computed with and without using the Hubbard-U correction for the Ti d-orbitals ($U = 2.5\text{eV}$).

Energy of formations at the vacancy and interlayer positions were computed for Li and Mg ions using both DFT and DFT+U. The Hubbard-U correction was chosen to be 2.5eV to be consistent with the recommendations from Hu and Metiu.¹ Structures are considered before relaxation, and thus the energies of formations, while similar, should not be directly compared with those in Figure 2.

References

- (1) Hu, Z.; Metiu, H. Choice of U for DFT+U Calculations for Titanium Oxides. *J. Phys. Chem. C* **2011**, *115* (13), 5841–5845. <https://doi.org/10.1021/jp111350u>.